Air Toxics Monitoring Pilot Project

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National Project

- EPA funded - $3 million - Initial Year
  - $2.5 for monitoring
  - $0.5 for data analysis
- Purpose
  - Help design national network
    - Location of sites
    - Frequency of sampling
    - Spatial variability
  - Verify modeling (e.g. CEP, NATA)

Project Locations

- 1 pilot in each EPA region
- 4 urban areas
  - Providence, RI (5 sites)
  - Tampa Bay, FL (6 sites)
  - Detroit, MI (8 sites)
  - Seattle, WA (6 sites)
- 6 smaller city/rural areas
  - San Juan, PR; Charleston, WV; Rio Rancho, NM; Cedar Rapids, IA; Grand Junction, CO; and San Jacinto, CA

Logistics- National Program

- Initial project one- year duration
- Roughly calendar year 2001
- Sampling frequency $\geq$ 1 in 12 days
- At least the 17 core pollutants
  - 9 VOCs
  - 2 carbonyls
  - 6 metals
- Standardized methods

Spatial Scales

- Microscale - Represents localized areas (several to 100 meters)
- Middle Scale - Areas up to several blocks (100 to 500 meters)
- Neighborhood Scale - Extended area with uniform land use (0.5 - 4 km)
- Urban Scale - Overall citywide conditions (4 to 50 km)

Providence Sites

- 5 sites- neighborhood scale
  - E. Providence PAMS/PM2.5 site
  - Urban LeaguePM2.5 site - urban residential
  - Pawtucket PM2.5/PM10 site - adjacent to I-95
  - Johnson & Wales Univ. - combination residential/industrial
  - West End - urban school/ residential/industrial area

Providence Pollutants - 9 Core VOCs

Benzene

1,3-Butadiene

Trichloroethylene

Carbon tetrachloride

1,2-Dichloropropane

Tetrachloroethylene

Vinyl chloride

Dichloromethane

Chloroform

7 “Max” VOCs

- Acrylonitrile - data quality?
- 1,2-Dibromoethane
- cis-1,3-Dichloropropene
- trans-1,3-Dichloropropene
- 1,2-Dichloroethane
- Ethylene oxide - data quality?
- 1,1,2,2-Tetrachloroethane

16 Other VOC HAPs

Chloromethane	MEK
Carbon disulfide	1,1,1-Trichloroethane
Chlorobenzene	MTBE
p-Dichlorobenzene	Styrene
Ethylbenzene	Toluene
1,1-Dichloroethane	Xylenes (o, m & p)
1,1-Dichloroethene	n-Hexane
2,2,4 Trimethylpentane	

Core Metals and Carbonyls

Metals (total)

Beryllium

Cadmium

Chromium

Lead

Manganese

Nickel

Carbonyls

Formaldehyde

Acetaldehyde

(Acetone)

Network Operation

- All sites May 19, 2001 - May 26, 2002
- Two sites in 2nd year
- One site in 3rd year
- Start-up issues - electricity, training
- 24-hour samples every 6th day
  - All pollutants, all sites

Diurnal Variation

- E. Providence PAMS/Toxics site
- No continuous VOC monitors
- June, July and August - 8 3-hour VOC samples collected per day
- October, January and May - 2 12-hour VOC samples per day
- 6:00 AM - 6:00 PM, 6:00 PM - 6:00 AM

Method - VOCs

- EPA Method TO-14a/15
- Summa Canisters
- Xontec canister samplers
- Temperature controlled enclosures
- Analysis on GC/MS

Method - Carbonyls

- EPA Method TO-11a
- Collection on DNPH traps
- Atec 100 sampling unit
- Temperature controlled shelter
- HPLC analysis

Methods - Metals

- Collection with PM10 sampler and TSP Hi-Vol sampler
- EPA Method IO-3 with ICAP/MS or ICAP analysis
- RI analysis done by RTI

Methods - Semivolatiles

- Semivolatile (e.g. PAH) sampling not performed in Rhode Island
- In other states, use EPA method TO-13A
- Filters and sorbent (e.g. PUF)
- Solvent extraction
- GC/MS analysis

Preliminary Data Availability

- VOCs
  - 49 sampling days 5/19/01-3/3/02
- Carbonyls
  - 56 sampling days 5/19/01-4/14/02
- Metals
  - 47 sampling days 5/19/01-2/25/02

Metals - ICP vs ICP/MS

- Tradeoff
  - ICP - lower cost
  - ICP/MS - lower detection limit
- Initial analyses used ICP/MS
- All metals except Be present in levels above ICP MDL

ICP vs ICP/MS (cont)

- Be concentrations often below ICP MDL
- Mean Be concentrations:
  - 0.004 - 0.006 ng/m^3 (PM-10)
  - 0.007 - 0.009 ng/m^3 (TSP)
- Be 10^{-6} cancer level - 0.4 ng/m^3
- Be not health-significant, others > ICP MDL, so switched to ICP

Metals Background Issues

- Quartz filters contain background concentrations of metals
- Mean metals in blanks as percentage of mean in samples:
  - Pb 1 %
  - Mn 3 - 4 %
  - Cd 9 - 16 %
  - Ni 14 - 21 %
  - Cr 55 - 71%

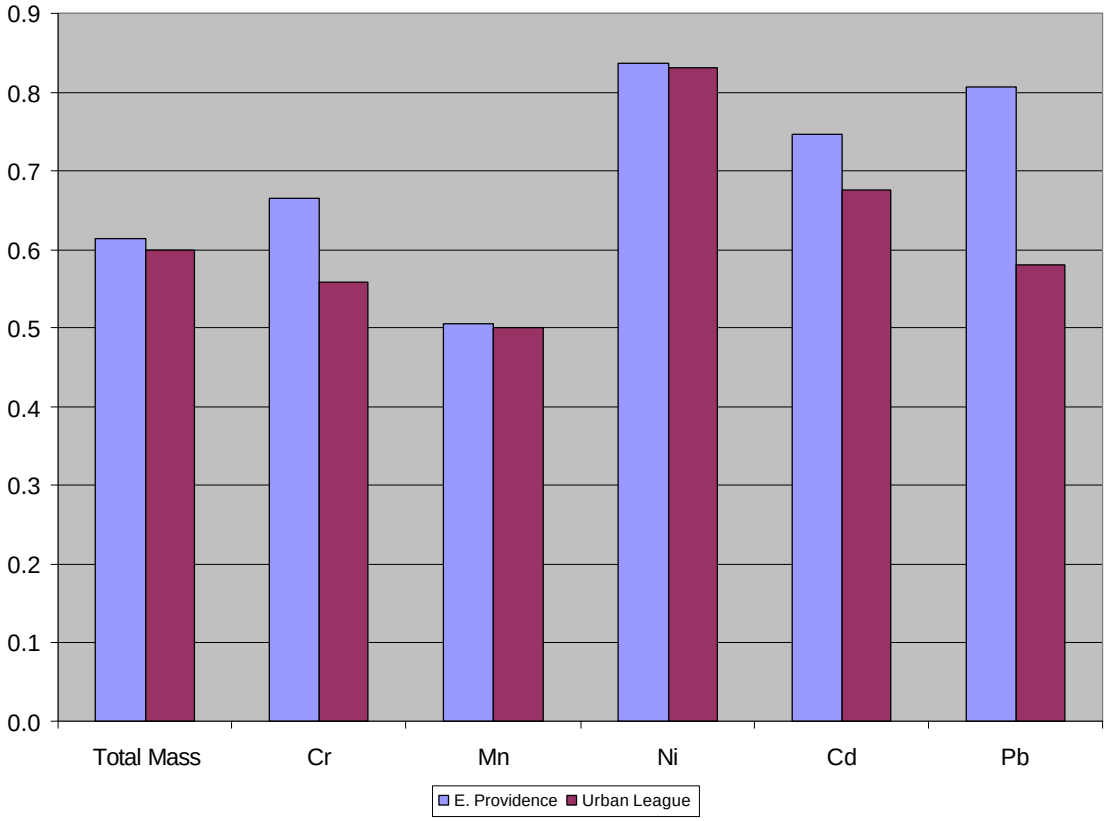
Comparison of Metals to Health Benchmarks (ng/m^3)

	Mean Conc.	Cancer BM	Non-cancer BM
Cr	0.5 - 1.1	0.08 (VI)	8
Mn	4.0 - 6.0		50
Ni	4.2 - 6.8	4	6000
Cd	0.2 - 0.4	0.6	
Pb	9.6 -12.1	80	1500

Chromium Issues

- Highest background levels on percentage basis (55-71%)
- Highest risk, assuming all is hexavalent (6 -14 X 10^{-6})
- California and Michigan have found low (3% and 1%) ratios of hexavalent to total chromium
- Highest levels of Cr (and Ni) at mobile source site

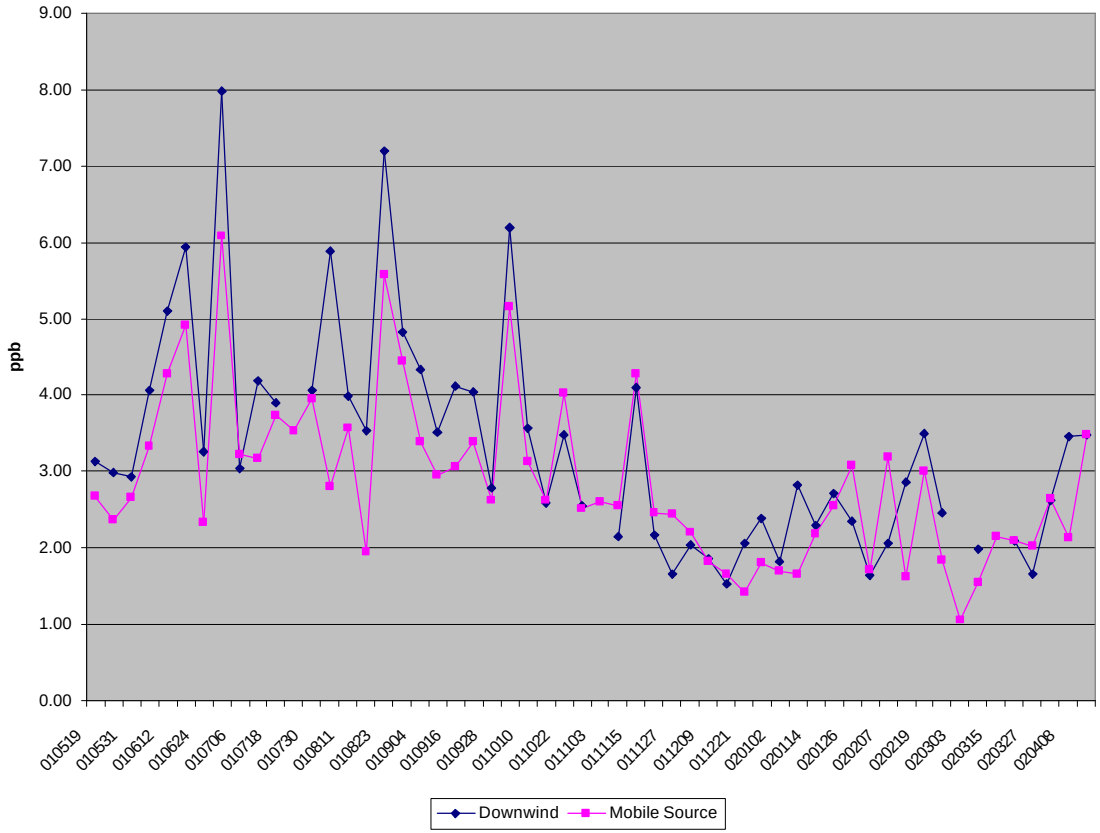
PM10 vs TSP


0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Total Mass
Cr
Mn
Ni
Cd
Pb
E. Providence
Urban League

Carbonyls at RI Sites

	(ppb)	(ppb)	
	Formaldehyde	Acetaldehyde	
Cancer BM	0.07	0.3	
NonCancer BM	30	5	
Average			
E Prov	3.3	1.1	
W End	3.1	1.0	
Pawtucket	2.9	0.9	
Urban Lg	2.9	0.9	
J & W	2.2	0.9	
Maximum			
E Prov	8.0	2.4	
W End	7.2	2.2	
Pawtucket	6.1	1.9	
Urban Lg	6.2	2.1	

Formaldehyde at Mobile Source and Downwind Sites



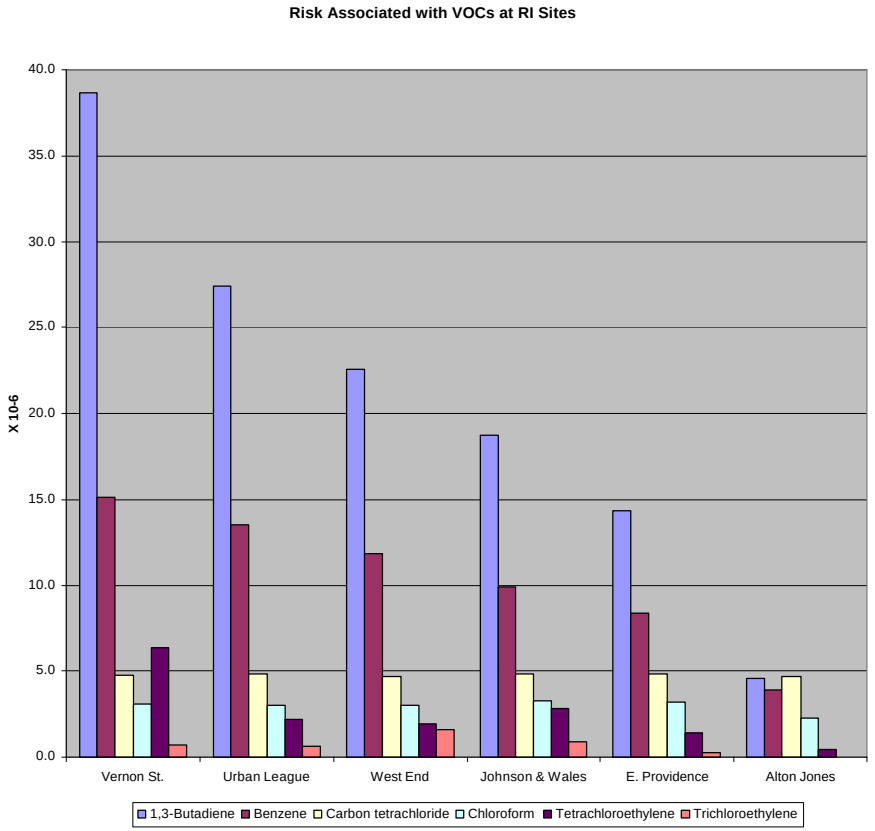
Carbonyl Issues

- Little spatial variability
- Downwind PAMs site levels $\geq$ levels at mobile source site
- Formaldehyde cancer risk at all sites 3 -5 X 10^{-5}
- Acetaldehyde cancer risk at all sites 3 X 10^{-6}
- Seasonality important

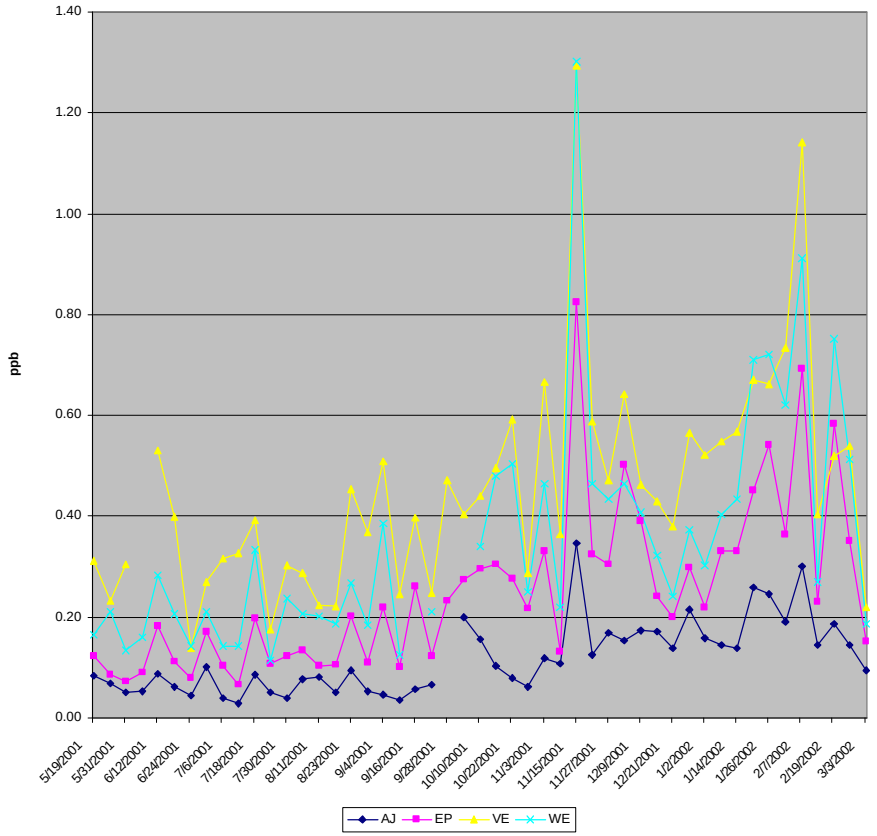
Highest Risk VOCs

- 1,3 butadiene $1 - 4 \times 10^{-5}$
- benzene $8 - 15 \times 10^{-6}$
- carbon tetrachloride 5×10^{-6}
- chloroform 3×10^{-6}
- tetrachloroethylene $1 - 6 \times 10^{-6}$
- trichloroethylene $0.2 - 2 \times 10^{-6}$

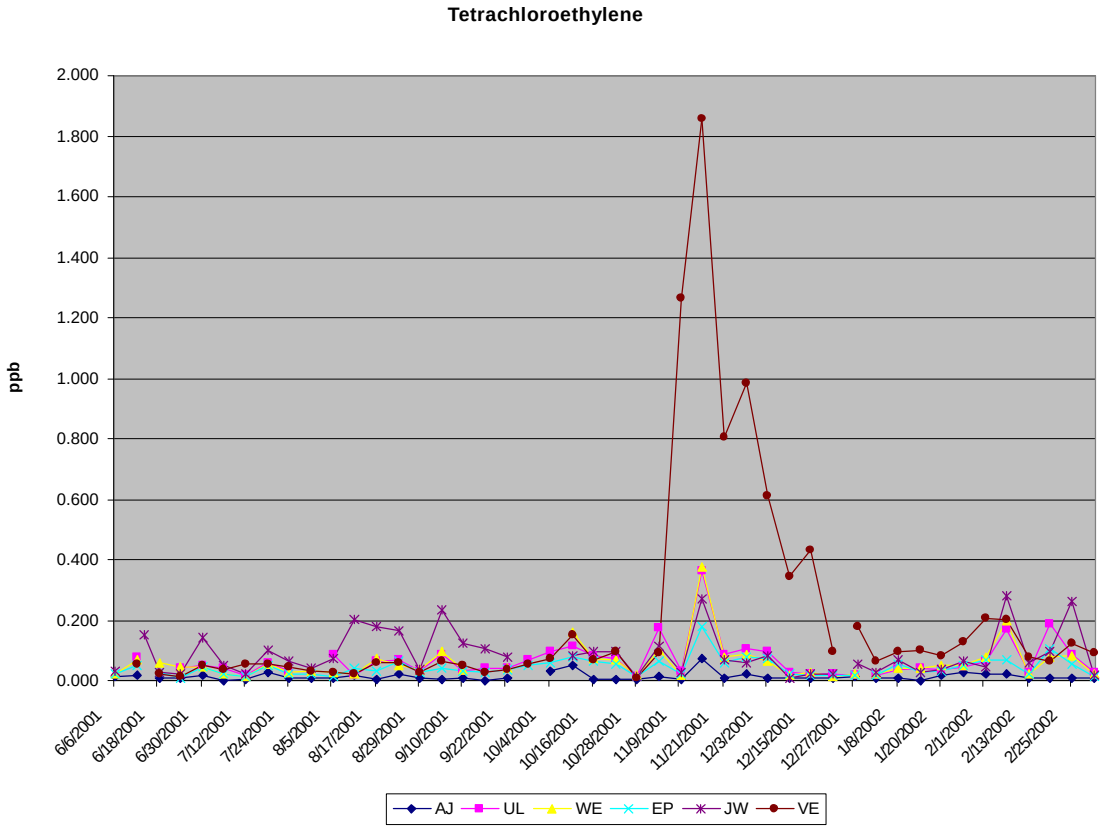
Risk from VOCs at RI Sites



Benzene Results (ppb)



Tetrachloroethylene Mystery



VOC Issues

- 6 VOCs exceed cancer benchmark
- 2 are from mobile sources, 2 background, and 2 from stationary
- acrylonitrile and ethylene oxide measurements not reliable
- benzene and 1,3-butadiene highest near highway, lowest in rural area

VOC Issues (cont)

- Very high levels of tetrachloroethylene seen at Pawtucket (mobile source) site for 6 weeks at end of 2001
- Difficult to pinpoint source, because of varying wind direction over 24-hour sampling period, lag time in sample processing
- May use sector sampling

Other Issues

- Need methods for measuring:
  - acrolien
  - acrylonitrile
  - ethylene oxide
  - diesel
  - arsenic

Other issues (cont)

- 24-hour formaldehyde (and acetaldehyde) peaks came close to short-term benchmarks.
- Continuous formaldehyde analysis would give more information.